

Message

From: Mark Strynar <[REDACTED]>
Sent: 2/4/2016 6:07:34 PM
To: Lindstrom, Andrew [/o=ExchangeLabs/ou=Exchange Administrative Group (FYDIBOHF23SPDLT)/cn=Recipients/cn=04bf7cf26aa44ce29763fbc1c1b2338e-Lindstrom, Andrew]; Strynar, Mark [/o=ExchangeLabs/ou=Exchange Administrative Group (FYDIBOHF23SPDLT)/cn=Recipients/cn=5a9910d5b38e471497bd875fd329a20a-Strynar, Mark]
Subject: Fwd: EPA response.
Attachments: Wang et al., 2013.pdf; USEPA (NERLRTP) sample collection and analysis protocols for perfluorina....pdf; Lindstrom SETAC 2014 .pdf; Heydebreck et al., 2015 New and legacy PFAS in Europe and China.pdf; The Madrid Statement on Poly- and Perfluoroalkyl Substances (PFASs).pdf; Nakayama et al. 2007.pdf

FYI

----- Forwarded message -----

From: "Sharon Lerner" <[REDACTED]>
Date: Feb 4, 2016 1:02 PM
Subject: Fwd: EPA response.
To: [REDACTED]
Cc: [REDACTED]

Sent from my phone

Begin forwarded message:

From: "Daguillard, Robert" <Daguillard.Robert@epa.gov>
Date: February 3, 2016 at 3:48:35 PM EST
To: Sharon Lerner <[REDACTED]>
Subject: EPA response.

Dear Sharon, here are the responses, for attribution to EPA. Thanks, R.

> How many water samples did they take?

The initial outing to collect samples for this effort included the collection of 9 samples. Additional follow-up samples were taken at select locations for confirmation at later time points (approximately 6 additional samples).

> Over what period of time?

The 9 initial samples were collected in a day in the summer of 2012. Follow-up samples mentioned above were collected infrequently in 2103 and 2014

> From what locations exactly?

The locations of the samples that were taken in the initial outing are found in Table S1 of the paper:

Table S1. Water samples description and 27 GPS coordinates.

Sample ID	Description	Latitude Longitude
CFR 001	Cape Fear river Tar Heel, NC	34.74525 -78.78574
CFR 002	Cape Fear river below Huske lock and dam #3	34.83026 -78.82246
CFR 003	unnamed tributary	34.83179 -78.82375
CFR 004	Cape Fear river above Huske lock and dam #3	34.83544 -78.82347
CFR 005	Cape Fear river below Rockfish creek	34.96820 -78.81579
CFR 006	Rockfish Creek	34.95610 -78.84424
CFR 007	Rockfish Creek WWTP effluent	34.96834 -78.82765
CFR 008	Cape Fear River at Fayetteville boat ramp access	34.99669 -78.85076
CFR 009	Regional drinking water sample	34.94199 -78.92422

Sometime between the summer of 2102 and in 2103 when follow-up samples were taken, CFR003 (unnamed tributary) ceased to be used as what appears to be an industrial outfall. It became evident that the industrial outfall was moved to above the Lock and Dam (CFR004) as this sample began to show compounds of interest with follow-up samples (2013 and 2014).

> How exactly did they get them (i.e. -using a boat, walking directly to the shore, etc).

All of the samples taken in this effort were by shore access. Samples were taken with a home-made dip sampler at points where the Cape Fear River was accessible to walk-in sampling from the bank. This generally was at public access points or bridge crossings of public roads to the water body being sampled. In one instance (CFR005) permission was asked of a local landowner to get access to the Cape Fear River for sampling. The one drinking water (CFR 009) sample was taken in the restroom at a local eating establishment.

> If it was a boat, can they please describe it?

A boat was not used for this effort.

> What sort of equipment did they use to analyze the samples?

The samples were concentrated using solid phase extraction (SPE). In this approach 0.5 liters of water is passed through a cartridge designed to capture potential compounds of interest, while allowing the water to pass through. The compounds of interest are selectively eluted with an organic solvent (methanol) and evaporated to 1.0 mL for analysis. The samples were analyzed using high performance liquid chromatography (HPLC) for compound separation coupled with Time-of-Flight Mass Spectrometry (TOFMS) for compound detection.

Question: How can this research be useful (i.e. how can scientists benefit from this information)?

Answer: *(Response from Andy Lindstrom, Ph.D., and Mark Strynar, Ph.D., scientists in EPA's National Exposure Research Laboratory)*

Because these 12 previously undescribed PFAS are closely related to PFAS that are known to have health and environmental risks, researchers should conduct toxicity and persistence studies to determine whether these materials have the same characteristics as the original long-chain PFAS. For environmental chemists, it's important to note that these new formulations include structures that are based on repeating units of CF₂O with an exact mass offset of 65.9917 m/z for members of this family of compounds. At this time, we are not aware of any research programs that are designed or funded to investigate these emerging concerns. More broadly, this paper provides confirmation that the major producers of PFAS have shifted their product design and production strategies and a new generation of replacement compounds is now out in the environment. Traditional PFCs have been shown to be difficult to remove via conventional drinking water processes. It is important to understand how well these new compounds are able to be removed via conventional drinking water process.

Additional background information provided by EPA's Office of Water:

This research identifies 12 previously undescribed PFAS in the environment and could be useful in identifying contaminants for the Unregulated Contaminant Monitoring Rule (UCMR) and Contaminant Candidate Lists (CCL). EPA is required under the Safe Drinking Water Act (SDWA) to publish a list of contaminants (the CCL) every 5 years that are not subject to any proposed or promulgated national primary drinking water regulation (NPDWR) which are known or anticipated to occur in public water supplies and may require regulation. EPA uses the CCL to identify priority contaminants for research on health effects and information collection on frequency and levels of occurrence in public water systems to determine if the contaminant should be regulated. The purpose of the UCMR is to collect occurrence data for contaminants suspected to be present in drinking water but that do not have health-based standards set under the SDWA.

Question: What research questions does this paper raise?

Answer: *(Response from Andy Lindstrom, Ph.D., and Mark Strynar, Ph.D., scientists in EPA's National Exposure Research Laboratory)*

Given that we document the presence of a dozen new PFAS in one river basin in North Carolina, this study raises a series of important questions. Are these found elsewhere in the US and around the world? What are the environmental and human health risks associated with these new materials? How can they be effectively removed from source water to ensure that they do not contaminate drinking water supplies?

Question: Do they bear notable similarities to other chemicals?

Answer: (Response from Andy Lindstrom, Ph.D., and Mark Strynar, Ph.D., scientists in EPA's National Exposure Research Laboratory)

The Strynar et al. publication has documented chemical structures that are both similar and different to the conventional legacy PFCAs and PFSA's. A notable difference is that the structures documented in the paper include an oxygen molecule, making them fluoroethers, which is different than the well known legacy perfluorinated carboxylic acids (PFCAs) and sulfonates (PFSA's), such as PFOA and PFOS, respectively. However, these ether chemicals do have carbon-fluorine bonds in common with legacy PFCAs and PFSA's that suggest that they are persistent. Their structural similarity to legacy fluorochemicals also suggest that they may be bioaccumulative, however, studies demonstrating this characteristic have not been conducted to date that we know of. Limited data and uncertainties about the persistence and bioaccumulation of fluorochemicals is the impetus for ongoing requests by EPA for testing under the TSCA New Chemicals Program.

Additional background information provided by EPA's Office of Chemical Safety and Pollution Prevention

Over the past decade, over 300 alternatives of various types for PFOA and other long-chain perfluorinated chemicals have been received and reviewed by EPA. Under the Toxic Substances Control Act (TSCA) New Chemicals program, EPA reviews the new substances to identify whether the range of toxicity, fate and bioaccumulation issues that have caused past concerns with long-chain perfluorinated substances (PFCs) may be present, as well as any issues that may be raised by new chemistries, in order to determine whether the new chemical presents an unreasonable risk to health or the environment. EPA's regulatory approach is intended to ensure that the new substances are safer alternatives prior to entering the market. At present, there are a range of short-chain PFCs (e.g., C6 and C4) that are available for use as substitutes. EPA's efforts to fully understand any potential risks continue.

Question: Where did they find these chemicals?

Answer: (Response from Andy Lindstrom, Ph.D., and Mark Strynar, Ph.D., scientists in EPA's National Exposure Research Laboratory)

We measured the 12 new per and polyfluoroalkyl substances (PFAS) identified in the paper in the Cape Fear River immediately above the William O. Huske lock and dam and downstream to Wilmington, NC (GPS coordinates of the sample points are given in Table S1 of the paper).

Question: How they knew to look for the chemicals where they did?

Answer: (Response from Andy Lindstrom, Ph.D., and Mark Strynar, Ph.D., scientists in EPA's National Exposure Research Laboratory)

We have been conducting research on the Cape Fear River for about ten years now. The primary reason we are looking in this area is that the EPA laboratory in Research Triangle Park is in the Cape Fear River watershed and we can travel to the river quickly to collect routine samples without difficulty. Our earlier research (published in Nakayama et al. *Environmental Science & Technology* 41, 5271-5276, 2007, attached) showed that the Cape Fear had many different sources of PFAS along its entire course. We have since documented sources related to effluents from waste water treatment plants, biosolid application areas, firefighting training areas, industrial effluents, and other as yet uncharacterized sources. In the Nakayama et al. paper we noted a large source at this specific location near the Huske lock and dam, most likely related to the nearby DuPont (currently Chemours) chemical facility that was at the time producing PFOA for use at DuPont's Washington Works facility in Parkersburg, WV.

Question: How exactly did they get the water samples? (i.e. a description of their process)

Answer: (Response from Andy Lindstrom, Ph.D., and Mark Strynar, Ph.D., scientists in EPA's National Exposure Research Laboratory)

We describe the water collection procedures in the 2007 Nakayama et al. paper. Briefly, we collected river water about a foot below the water's surface from shore using a homemade dip sampler and from bridges using a long rope and a stainless steel Kemmerer sampler. The procedures are described in the attached PowerPoint presentation entitled "USEPA (NERL/RTP) sample collection and analysis protocols for perfluorinated compounds in surface and well water" which was presented at an Environment

Canada workshop entitled “Federal Contaminated Sites Action Plan Management of Perfluorinated Compounds at Federal Contaminated Sites” in Ottawa Canada, February 19-20, 2014.

Question: Once they got samples, how did they figure out which chemicals were in the water?

Answer: *(Response from Andy Lindstrom, Ph.D., and Mark Strynar, Ph.D., scientists in EPA’s National Exposure Research Laboratory)*

This is one of the major points of the paper – how to find previously undescribed PFAS in samples.

Figure 1 in the paper is a good high level summary of our process. First (step 1) we go to a location where there is a suspected source and collect samples from above and below this hypothetical input site. In step 2 we analyze these samples using nontargeted time of flight mass spectrometry (TOFMS). This is a broad screening analytical method that measures the accurate mass of each observable compound in the sample. The instrument software then allows us to subtract signals seen in the upstream sample (uncontaminated river water) from the downstream sample (river water plus input from the specific source) giving only the major compounds coming from the suspected input source (step 3). In step 4 instrument background noise is removed from the raw data and then a program is used generate likely molecular formulae (e.g., $C_6HF_{11}O_3$) for each identifiable compound found in the sample. It is important to note here that each atom in nature has a very specific weight (e.g., C = 12.000, F = 18.998, H = 1.007, etc.) so if you know the accurate mass of the entire compound, the computer can figure out the most likely combination of atoms needed to come up with this accurate mass. In step 5 the analyst uses a variety of techniques to sort through these data to confirm the most likely computer generated formula for each compound, to propose specific structures and compound identities (there are often many possible ways to arrange the atoms identified in the accurate mass formulation), and to identify “families” of related compounds that may be present in the sample. We specifically point out here that PFAS can often be identified by their negative mass defect (a molecular weight that is slightly less than a whole number, like 329.9750 m/z for $C_6HF_{11}O_3$), and members of a specific family of PFAS may have the same basic structure but differ from one another by being longer or shorter with the addition or subtraction of CF_2 or CF_2O units (see Figure 2b and Figure S5).

A major finding of this work is the identification of new PFAS that incorporate CF₂O units. Members of this family of compounds will differ from one another by a mass of 65.9917 *m/z* (Figure 2B), and this work makes it apparent that chemical manufacturers are now using this type of structure for some of the materials they produce. In a related paper, another group (Wang et al., *Environment International* (60) 242-248 2013) has shown that other new PFAS formulations are being manufactured using repeating units of C₂F₄O and C₃F₆O. Because all of these new formulations contain internal ether oxygen atoms, the resulting new materials are not technically classified as being “long-chain perfluorinated compounds”, which have seven or more repeating CF₂ units. Instead, these newer compounds have repeating CF₂O units (for example) and are therefore technically permissible under the EPA’s Stewardship agreement and other international regulations. However, because the basic chemical structure is the same (long chain fatty acid-like materials), including repeating units of carbon bound to fluorine, one would expect the same chemical performance properties with these new compounds. This would also suggest that their toxicity and environmental persistence are likely to be similar as well. The limited amount of research that has been published on these new types of PFAS compounds suggests that in most critical respects they are very similar to the corresponding substances that they are meant to replace. A good overview of the current situation concerning the production and regulation of the PFAS can be found in The Madrid Statement on Poly- and Perfluoroalkyl Substances (PFASs) (*Environmental Health Perspectives*, 123 (5) A107-A111, 2015, attached).

Question: How can this research be useful (i.e. how can scientists benefit from this information)?

Answer: (Response from Andy Lindstrom, Ph.D., and Mark Strynar, Ph.D., scientists in EPA’s National Exposure Research Laboratory)

Because these 12 previously undescribed PFAS are closely related to PFAS that are known to have health and environmental risks, researchers should conduct toxicity and persistence studies to determine whether these materials have the same characteristics as the original long-chain PFAS. For environmental chemists, it’s important to note that these new formulations include structures that are based on repeating units of CF₂O with an exact mass offset of 65.9917 *m/z* for members of this family of compounds. At this time, we are not aware of any research programs that are designed or funded to investigate these emerging concerns. More broadly, this paper provides confirmation that the major producers of PFAS have shifted their product design and production strategies and a new generation of replacement compounds is now out in the environment. Traditional PFCs have been shown to be difficult to remove via conventional drinking water processes. It is important to understand how well these new compounds are able to be removed via conventional drinking water process.

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Question: What research questions does this paper raise?

Answer: *(Response from Andy Lindstrom, Ph.D., and Mark Strynar, Ph.D., scientists in EPA's National Exposure Research Laboratory)*

Given that we document the presence of a dozen new PFAS in one river basin in North Carolina, this study raises a series of important questions. Are these found elsewhere in the US and around the world? What are the environmental and human health risks associated with these new materials? How can they be effectively removed from source water to ensure that they do not contaminate drinking water supplies?

Question: What is known about the chemicals you found?

Answer: *(Response from Andy Lindstrom, Ph.D., and Mark Strynar, Ph.D., scientists in EPA's National Exposure Research Laboratory)*

We are not aware of any additional published information regarding the majority of the new compounds described in this paper. The $C_6HF_{11}O_3$ compound is known as undecafluoro-2-methyl-3-oxahexanoic acid (CAS number 13252-13-6 or GenX), and there is limited published information available concerning its toxicity and environmental persistence. These studies have shown no potential for degradation under normal environmental conditions and similar types of toxicity compared to the legacy PFAS.

Additionally a new study by Heydebreck et al. (*Environmental Science and Technology* (49) 8386-8395, 2015, attached) has confirmed the presence of one of the compounds we identified in water samples from Asia and Europe.

Question: Do they bear notable similarities to other chemicals?

Answer: *(Response from Andy Lindstrom, Ph.D., and Mark Strynar, Ph.D., scientists in EPA's National Exposure Research Laboratory)*

As indicated above, the new chemicals that we have documented in this work are very similar to the conventional legacy PFAS. The chemical properties in both groups of compounds come from the presence of carbon-fluorine bonds so it is reasonable to expect that the new compounds will behave similarly to the legacy pollutants. It is important to note that most of these compounds have not been described in the literature.

Question: Are there any presentations I might see, powerpoints or something, else that summarize their process or findings?

Answer: *(Response from Andy Lindstrom, Ph.D., and Mark Strynar, Ph.D., scientists in EPA's National Exposure Research Laboratory)*

We have attached the following PowerPoint presentations that have presented at conferences to provide background information for this manuscript:

“USEPA (NERL/RTP) sample collection and analysis protocols for perfluorinated compounds in surface and well water” Environment Canada workshop entitled “Federal Contaminated Sites Action Plan Management of Perfluorinated Compounds at Federal Contaminated Sites” Ottawa Canada, February 19-20, 2014.

“Surface Disposal of Waste Water Treatment Plant Biosolids – an Important Source of Perfluorinated Compound Contamination in the Environment?” SETAC North America, Vancouver, BC, Canada

November 9-13, 2014.

“Determination of perfluoroalkyl ether carboxylic acids (PFECAs) and sulfonic acids (PFESAs) in North Carolina surface water using high resolution mass spectrometry” SETAC North America, Vancouver, BC, Canada November 9-13, 2014.

Question: Do they have CBI clearance? Why or why not?”

Answer: (Response from Andy Lindstrom, Ph.D., and Mark Strynar, Ph.D., scientists in EPA’s National Exposure Research Laboratory)

We currently don’t have CBI clearance for TSCA or FIFRA related materials.

How many hours would they estimate they spent analyzing the samples and doing other work for the paper?

This is a very difficult question to answer as this initial effort started in the summer of 2012 and lasted until late in the year 2014 with some follow-up samples. The overwhelming majority of this time was spent looking at data files that were run on the HPLC-TOFMS and determining potential structures from accurate mass peaks. This was a slow and pains-taking process that involved a lot of learning as we progressed in the research. We think a conservative estimate would be at least 100 hours was spent on this effort, however it is likely it was much more than that.

1) In their paper (page E) they say there were "77 features that were unique to the downstream sample." Does that mean there were 77 chemicals that were not in the upstream sample and were in the downstream sample? If not, can they please clarify.

A feature is defined as 1) an accurate mass, 2) a retention time and 3) an abundance measurement (integrated area under a peak). These three things define a feature. However, there is not a one to one correlation between a feature and a chemical. For instance four features could all be related to the same chemical (a fragment, the parent compound, a sodiated dimer and a protonated dimer). All of these four features would point back to one chemical. Thus the “77 features” does not necessarily mean 77 chemicals.

2) What is known about the relative stability of these PFCs (whose carbon chains are separated by oxygen atoms) to for instance PFOA?

Very little is known about the degradability of these PFECAs (perfluoroether carboxylic acids). According to Wang et al. 2013 they are quite persistent, however they have limited data. ADONA refers to a 3M compound and GenX to a DuPont (now Chemours) compound. Here is a quote from their paper:

“For PFPE-based alternatives, information on degradability is scarce and often incomplete. Available information shows that ADONA is not readily biodegradable (Gordon, 2011), but starts to decompose thermally at 125 °C with completion at 175 °C, leading to formation of volatile substances (details on degradation products were not provided) (EFSA, 2011b). No hydrolysis and biodegradability of GenX was observed in tests according to the OECD test guidelines 111 (tested at pH = 4, 7, 9 at 50 °C) and 301B (tested for up to 28 days), respectively (ECHA, 2013b).” (see reference Below)

What do we know about how much less stable - and thus less persistent - they are?

Any claims about less persistence or less stability of these perfluoroether compounds has not been shared in the peer reviewed literature.

Reference:

Fluorinated alternatives to long-chain perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs) and their potential precursors. ZhanyunWang, Ian T. Cousins, Martin Scheringer, Konrad Hungerbühler. *Environment International* 60 (2013) 242–248.

Robert Daguiard

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